

Raman Mapping of Carbonates in ALH84001 Martian Meteorite. M.S. Bell¹, J. McHone², A. Kudryavtsev², and D.S. McKay³, ¹University of Houston/Lockheed-Martin, Houston, TX, msbell@ems.jsc.nasa.gov, ²U. of Alabama - Birmingham, ³NASA/Johnson Space Center, Houston, TX.

Introduction: The shock history of ALH84001 includes at least two impact events: one in which the cumulate rock was brought to the surface of Mars and one in which it was ejected from the planet [1]. Bell et al. [2] have used TEM to examine small amounts (tens of nanometer sized patches) of amorphous pyroxene and silica in ALH84001 which are possible incipient shock products. However, spatial distribution of these phases is difficult to determine on the nanometer scale and ultramicrotome preparation of samples can juxtapose phases, that were not originally related. In addition, Brearly [3] and Scott et al. [4] have suggested that magnetite crystals in Martian meteorite ALH84001 that are associated with void space in the carbonate globules were produced by thermal decomposition of the carbonate at high temperature, possibly by incipient shock melting or devolatilization. This process should produce MgO and CaO from the breakdown of the magnesian carbonate but these phases have not been reported. In an effort to further constrain the effects of shock metamorphism experienced by ALH84001 both during transport to the surface of Mars and ejection from the planet, carbonate globules and surrounding orthopyroxene were examined for oxides and traces of amorphous phases by Raman spectroscopic mapping.

Experimental procedure: Raman was chosen for several reasons, all of which are important for rare and environmentally sensitive samples. The in-situ process of data acquisition is non-destructive and requires no sample contact. This prevents the possibility of contamination. No coatings are applied so no surface artifacts are induced which may influence subsequent analyses. Concentrations can be detected in the range of PPM. Raman allows for the identification of different molecules because the relative wave number shift for a particular molecule is constant. Finally, analysis is fast.

A flat area of an unprepared ALH chip surface 90 μm x 90 μm containing two intergrown carbonates and orthopyroxene (Fig. 1) was mapped. A Dilor XY triple stage Raman system with macro, confocal micro and line scan imaging options in the U. of Alabama – Birmingham Lab was utilized. Data acquisition was controlled by LabSpec v. 2.09 software. An Innova90 Kr+ ion

laser operated at 23 mW with a 2 μm spot diameter. Radiation was collected in back-scattering geometry with a data collection interval of 3 μm X 3 μm , a 50s acquisition time, and a slit width of 200 μm . Standards and sample were analyzed under the same experimental conditions at room temperature (20°C) and 1st order Stokes Raman scattering was recorded.

To produce a Raman map, characteristic peaks in Raman spectra were identified from reference spectra to define the spectral window. The map produced displays the distribution and intensity (as brightness) of that peak in the area of interest.

Results: In carbonate, the libration lattice mode vibration in the wave number range 270 – 345 cm^{-1} is the peak which is sensitive to the cation. Figure 2 is a map of the characteristic 330 cm^{-1} magnesite peak. This map locates a band of magnesite on the outer margin of the carbonate. A peak at 312 cm^{-1} in the carbonate spectra intermediate to the magnesite and the siderite (282 cm^{-1})/calcite (288 cm^{-1})/rhodocrosite (291 cm^{-1}) peaks is mapped in figure 3. Solid solution carbonate for the 312 cm^{-1} peak (probably Fe-rich) is heterogeneously distributed in the rosette interior as indicated by intensity variation in that region. This variation has been quantified by electron microprobe mapping of carbonates zoned from Ca, Mn rich cores to more Fe then Mg rich rims [5]. Spectra obtained from the carbonate interior and rim for the lattice mode spectral region are in agreement with those obtained by Cooney et al. [6]. However, our internal mode peaks (C-O stretch) are slightly higher in wave number for both the rim (1095 cm^{-1}) and core (1091 cm^{-1}). Figure 4. is the spectra obtained for the bright region at the arrows in figure 5. The peak at 690 cm^{-1} is the most intense magnetite vibration mode and overlaps the orthopyroxene 660 cm^{-1} and 667 cm^{-1} doublet. For this reason, the Raman map produced from this spectral window has bright regions of magnetite inside the magnesite rim and of pyroxene surrounding the carbonate. The 690 cm^{-1} magnetite peak is broadened due to the small size of the magnetite particles [7]. In addition, this region contains a high silica content phase (470 cm^{-1}) previously reported to be amorphous silica [8].

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This peak is broadened but better defined than for an amorphous phase.

Conclusions: Raman mapping (resolution ~1-2 cm⁻¹) detected no micron-sized pyroxene or silica glasses in this area. CaO and MgO produce strong and distinct Raman signals that also were not detected in the ALH carbonate. If the pre-shock ALH carbonate was siderite, it is conceivable that shock metamorphism could produce magnetite and leave no residual oxides.

References: [1] Treiman A. H. (1995) *Meteoritics* 30, 294-302. [2] Bell et al. (1999) LPSC XXX, #1951, CD-ROM. [3] Brearly A. (1998) LPSC XXIX #1451, CD-ROM. [4] Scott et al. (1997) *Nature* 387, 377-379. [5] McKay and Lofgren (1997) LPSC XXVIII #1799, CD-ROM. [6] Cooney et al. (1999) *Amer. Min.* 84, 1569-1576. [7] Thomas et al. (1998) LPSC XXIX #1494, CD-ROM. [8] Bell et al., (1999) GSA Annual Meeting, .31, 7, A45.

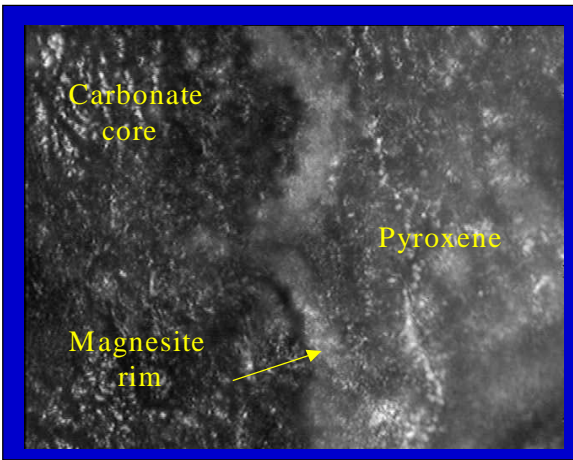


Fig. 1 Optical image of map area, 90 μm x 90 μm.

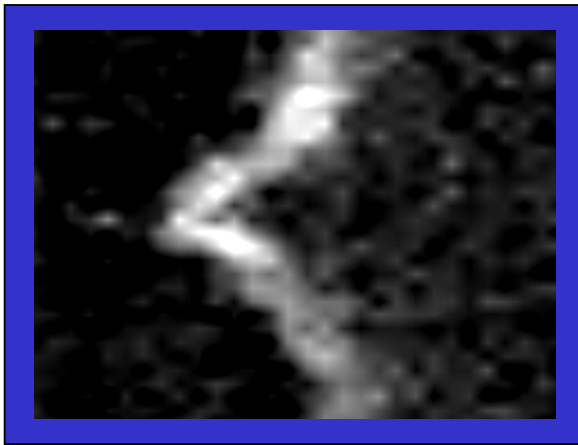
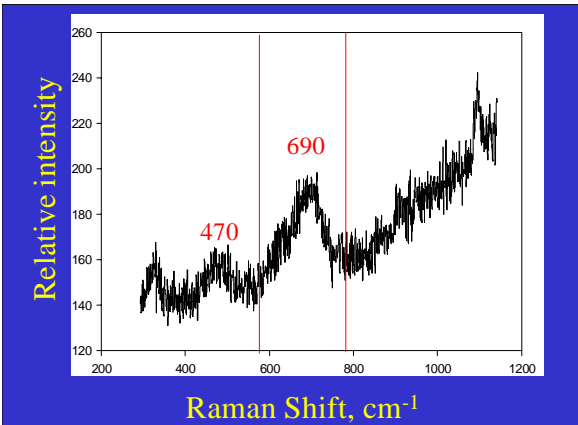


Fig. 2. Raman map of magnetite rim. Brightest areas record highest intensity for a given peak.

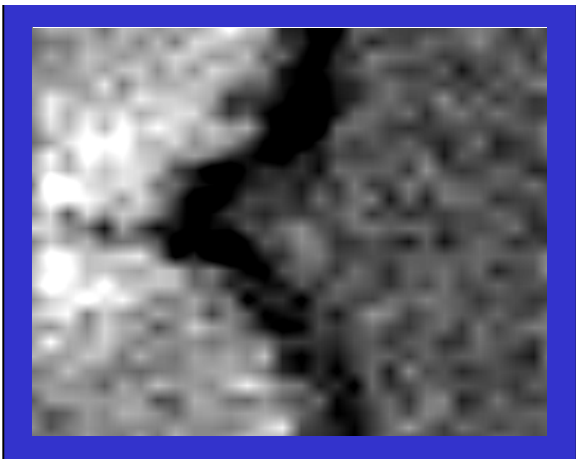


Fig. 3. Raman map of Carbonate solid solution in core (brightest region on left of image).

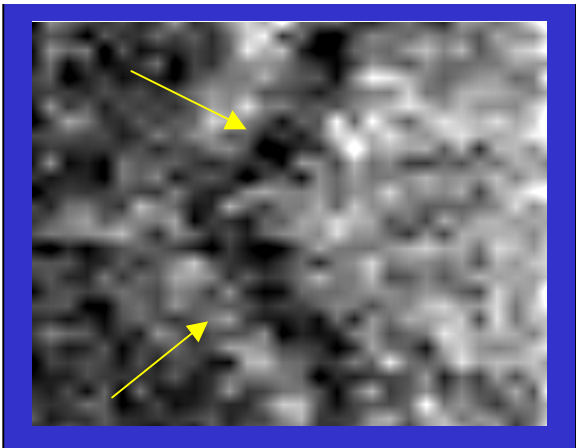


Fig. 5. Raman map of magnetite and silica phase between rim and core (arrows).

Fig. 4. Raman spectra of magnetite window (667) and silica phase (470) mapped in Fig.5.